1. \( \text{Ag}^+ + e^- \rightarrow \text{Ag} \), so 1 mol of \( e^- \)s \( \rightarrow 1 \) mol \( \text{Ag} \)
\[
8.95 \times 10^{-3} \text{ mol} = 8.297 \times 10^{-5} \text{ mol}
\]
\[
\therefore I = \frac{nF}{t(s)} = 8.005 \text{ C}.
\]
\[
I \text{ (amps)} = \frac{A \text{ (C)}}{t(s)} = 8.005 \text{ C} = 24.00 \text{ s} = 3.336 \times 10^{-3} \text{ A}
\]

For simple product/ division relationships, error propagation gives
\[
(\text{error})^2 = \left( \frac{\text{error}}{A} \right)^2 + \left( \frac{\text{error}}{C} \right)^2 + \left( \frac{\text{error}}{\text{C}} \right)^2
\]
\[
= \left( \frac{0.01}{8.95} \right)^2 + \left( \frac{6.1}{2400} \right)^2
\]
\[
= (1.12 \times 10^{-3})^2
\]
Thus, \( I = (3.36 \pm 0.004) \times 10^{-3} \text{ A} \) (also written as \( I = 3.36 (4) \times 10^{-3} \text{ A} \)).

2. \( \text{Pt}_1 | \text{H}_2(g) | \text{HBr (aq)} | \text{AgBr (s)} | \text{Ag}^+ (aq) | \text{Ag} (s) | \text{Pt}_2 \)

The "simple" solution for \( E^\circ \) is \( E^\circ = E^\circ\text{R} = E^\circ\text{L} = 0.771 \text{V} \), where the numerical value comes from Table 14.1 for the \( \text{Ag}^+ | \text{Ag} \) electrode. (Then one does not need the solubility information.)

Alternatively, consider the cell,

(b) \( \text{Pt}_1 | \text{H}_2(g) | \text{HBr (aq)}, \text{Ag}^+ (aq) | \text{Ag} (s) | \text{Pt}_2 \).

In cell (a), \( E_a = E_a^\circ - \frac{RT}{\text{mol}} \ln \frac{a(\text{H}^+)}{a(\text{H}_2)} \)

\( (w/ \ a(\text{Ag}) \approx a(\text{AgBr}) \approx 1) \), \( E = E^\circ \) when all \( a(S) = 1 \).

In (b), the cell \( \text{Rx} \) is \( \frac{1}{2} \text{H}_2(g) + \text{Ag}^+ (aq) \rightarrow \text{H}^+ (aq) + \text{Ag} (s) \), and \( E_b = E_b^\circ - \frac{RT}{\text{mol}} \ln \frac{a(\text{H}^+)}{a(\text{Ag}^+)a(\text{H}_2)} + E_b^\circ = 0.799 \text{V} \)

2. (cont.) The \( E^\circ \) value is for the \( \text{Ag}^+ | \text{Ag} \) electrode.

But \( a(\text{Ag}^+) \) is limited by \( K^\circ = a(\text{Ag})a(\text{Br}^-) \).

Thus \( E^\circ = E_b^\circ - \frac{RT}{\text{mol}} \ln \frac{a(\text{H}^+)}{a(\text{H}_2)} K^\circ \)

\( = E_b^\circ - \frac{RT}{\text{mol}} \ln \frac{a(\text{H}^+)}{a(\text{H}_2)} - \frac{RT}{\text{mol}} \ln \frac{a(\text{H}^+)}{a(\text{H}_2)} \frac{a(\text{Ag})a(\text{Br}^-)}{a(\text{Ag}^+)a(\text{Br}^-)} \)

\( = E_b^\circ - \frac{RT}{\text{mol}} \ln \frac{a(\text{H}^+)}{a(\text{H}_2)} \frac{a(\text{Ag})a(\text{Br}^-)}{a(\text{Ag}^+)a(\text{Br}^-)} \)

Now \( K^\circ = \gamma^2 \frac{m^2}{n^2} = \gamma^2 (2.10 \times 10^{-4})^2 \).
i.e. \( E_b^\circ = 0.997 \text{V} \), whose \( K^\circ = 4.40 \times 10^{-12} \text{V} \)

giving \( E_b^\circ = 0.799 - 0.672 = 0.127 \text{V} \).

The agreement \( w/ \ E_b^\circ = 0.071 \text{V} \) is not as good as might be hoped for. In fact, I have found a tabulated \( K^\circ \) value of \( 7.7 \times 10^{-13} \text{V} \) for \( \text{AgBr} \), from which \( E_b^\circ = 0.082 \text{V} \), in much better agreement. Evidently the solubility given in the problem is wrong.

A third approach is that of Davies's problem 14.38, which obtains \( E^\circ \) for the \( \text{Ag}^+ | \text{AgI} \) electrode by driving a cell having its \( K^\circ = K^\circ \).

Then \( E^\circ = \frac{RT}{\text{mol}} \ln K^\circ / n \) \( \text{F} = E_b^\circ - E_b^\circ \), from which the missing half cell \( E^\circ \) value is calculated.
3. (a) \[ \text{Left: } Ag + I^- \rightarrow AgI + e^- \]
\[ \text{Right: } \frac{1}{2} I_2 + e^- \rightarrow I^- \]
\[ \text{Net: } Ag + \frac{1}{2} I_2 \rightarrow AgI \]

(b) \[ E^0 = E^0_R - E^0_L = 0.536 V - (-0.152 V) = 0.688 V \]

(c) \[ \Delta S^0 = nF \frac{\partial E^0}{\partial T} = 1 \times 96485 C \times 10^{-3} V K = 9.65 \text{ J/K/mol} \]
\[ \Delta G^0 = -nF \Delta E^0 = -66.38 \text{ kJ/mol} \]
\[ \Delta H^0 = \Delta G^0 + T \Delta S^0 = -63.50 \text{ kJ/mol} \]

4. (a) \[ \text{Left: } Na \rightarrow Na^+ + e^- \quad Na, Hg | NaCl(aq) | AgCl | Ag \]
\[ \text{Right: } AgCl + e^- \rightarrow Ag + Cl^- \]
\[ \text{Net: } AgCl + Na \rightarrow Ag + Na^+ + Cl^- \]
\[ E^0 = E^0_R - E^0_L = 0.222 - (-2.71) V = 2.93 V \]

(b) \[ E = E^0 - \frac{RT}{F} \ln a(\text{NaCl}) \]
\[ E_L = E^0 - \frac{RT}{F} \ln a(L) \quad (L = \text{left}) \]
\[ E_R = E^0 - \frac{RT}{F} \ln a(R) \]
\[ E = E_R - E_L = \frac{RT}{F} \ln \frac{a_{\text{Ag}}}{a_{\text{Ag}}} = \frac{RT}{F} \ln \left( \frac{\gamma_{\text{Ag}}^2 (0.0001)}{\gamma_{\text{Ag}} (0.102)} \right) \]
\[ E = \frac{2RT}{F} \left( \ln 0.1 + \frac{\gamma_{I^2}^2}{\gamma_{I^2}} \right) \]
\[ E(35^\circ C) = 0.19755 V \quad \frac{\gamma_{I^2}}{\gamma_{Ag}} = 1.032 \]

Note: The net cell reaction here is \[ NaCl(aq, L) \rightarrow NaCl(aq, R) \]

5. \[ \text{Left: } I^- \rightarrow \frac{1}{2} I_2 + e^- \]
\[ \text{Right: } I_3^- + 2e^- \rightarrow 3 I^- \]
\[ E = E^0 - \frac{RT}{F} \ln \frac{a(I^2)}{a(I_3^-)} \]
\[ \text{Net: } I_3^- \rightarrow I_2 + I^- \]
\[ E_0 = E_R - E_L = 0.0010 V \]

At equilibrium, \[ E = 0 \]
\[ E = \frac{RT}{F} \ln \frac{a(I^2)}{a(I_3^-)} \]

\[ \Rightarrow \quad \frac{a(I^2)}{a(I_3^-)} = 1.081 \times \frac{m(I^2)}{m(I_3^-)} \]
\[ \Rightarrow \quad m(I_3^-) = 0.463 m^2 \text{ when } m(I^2) = 0.500 m^2. \]

Note: Since the solution is saturated with \( I_2 \) (and since we assume no water is dissolved in the solder \( I_2 \)), \( \mu; (I_3, Ag) = \mu^*(I_3, Ag) \); hence \( a(I_3, Ag) = 1.00 \).

6. \[ \text{Left: } Pb + S_2O_3^{2-} \rightarrow PbSO_4 + 2e^- \]
\[ \text{Right: } Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-} \]
\[ \text{Net: } Pb + Hg_2SO_4 \rightarrow 2Hg + PbSO_4 \]

A possible cell is \( Pb | PbSO_4 | Hg_2SO_4(aq) | Hg_2SO_4 | Hg \).

Since both electrodes are included in Table 14.1, the "easy" answer for \( E \) is \( E_R - E_L = 0.974 V \).

Alternatively, the cell may be considered as \( Pb | Pb^{2+}, SO_4^{2-}, Hg^{2+}, Hg | PbSO_4 \), having \[ E = E^0 - \frac{RT}{F} \ln \frac{a(Pb^{2+})}{a(Hg^{2+})} \quad ; \quad E^0 = 0.796 + 0.126 V \]

\[ K_{sp} [PbSO_4] = a(Pb^{2+})a(SO_4^{2-}) = 2.43 \times 10^{-8} \geq a(Pb^{2+}) \]
\[ K_{sp} [Hg_2SO_4] = a(Hg^{2+})a(SO_4^{2-}) = 1.46 \times 10^{-6} \geq a(Hg^{2+}) = K_{sp}(Hg_2SO_4) \]
\[ \Leftrightarrow E = 0.922 V - \frac{RT}{F} \ln (0.0168) = 0.975 V \]
7. \[ \text{Left: } \frac{1}{2} \text{H}_2 \rightarrow \text{H}^+ + e^- \]
   \[ \text{Right: } \frac{1}{2} \text{Cl}_2 + e^- \rightarrow \text{Cl}^- \]
   \[ \text{net: } \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 \rightarrow \text{H}^+ + \text{Cl}^- \]
   \[ E = E^0 - \frac{RT}{2F} \ln \left(\frac{a(\text{H}^+)}{a(\text{H}_2)} \right) \]
   \[ \text{where: } a(\text{H}_2) \approx \gamma \left(0.01\right)^2 \]
   \[ \gamma = 0.962 \]
   \[ \text{and: } a(\text{Cl}_2) \approx 1 \]

   \[ P(\text{H}_2) = 1 \text{ atm, so } a(\text{H}_2) \approx 1.00 \]

   \[ S E = E^0 - \frac{2RT}{F} \ln (\gamma x 0.01) \]
   \[ + \frac{RT}{F} \ln (\phi_{\text{Cl}_2}/\phi_{\text{Cl}^-}) \]
   \[ E = 1.359 \text{ V} - (-0.242 \text{ V}) \]
   \[ + \frac{RT}{F} \ln (\phi_{\text{Cl}_2}/\phi_{\text{Cl}^-}) \]

8. \[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}(l) \]

   Without knowing the cell design, we can always calculate a maximum possible work for an ideal reversible cell using:
   \[ \Delta G^0 = -nF \Delta E^0 \]

   Here, \[ \Delta G^0 \text{ (Levine Appendix) } = -56.687 \text{ kcal/mole} \]
   with \[ n = 2, \quad E^0 = 1.229 \text{ V} \]

   \( \text{(b) The maximum electrical work done in the combustion of } \text{H}_2 \text{ is } -\Delta G^0 \text{ for } 1 \text{ mole of } \text{H}_2 \approx 56.687 \text{ kcal/mole} \)

   \( \text{(c) Maximum heat (constant } P, T) = -\Delta H^0, \text{ which is given as } +68.315 \text{ kcal/mol} \)

   \( \text{(d) The maximum } \Delta \text{ total work is } -\Delta A^0. \text{ Since } \)
   \[ \Delta A = \Delta G - \Delta (\text{flow}) \equiv \Delta G - \Delta n_{\text{flow}}RT \]
   \[ \text{with } \Delta n_{\text{flow}} = -\frac{3}{2} \text{ mol here, } \Delta A^0 = -55.798 \text{ kcal} \]
   \[ \text{work obtained } = +55.798 \text{ kcal} \]

Note that obtainable work and heat are the negatives of the appropriate thermo functions, because the latter are defined as added to the system. Note also that the maximum total work is less than the electrical work! This is because work of compression is done on the system and is effectively added to \( \Delta A^0 \) to yield the electrical work, \( \Delta G^0 \).